

1122.545



# PATENT SPECIFICATION

NO DRAWINGS

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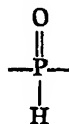
## COMPLETE SPECIFICATION

### Polyurethane Plastics

We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT**, a body corporate organised under the laws of Germany of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The production of high molecular weight cross-linked polyurethane plastics from linear or branched condensation- or polymerisation products containing hydroxyl groups and having a molecular weight over 1000 and polyisocyanates is already known. It is also known in the art to include in these polyaddition reactions compounds which contain at least two hydrogen atoms reactive with isocyanates and which have a molecular weight below 1000 that is so-called chain-lengthening agents, e.g. water, polyhydric alcohols or diamines.

The present invention provides a process for the production of high molecular weight cross-linked polyurethane plastics, which is characterised in that linear or branched polyurethanes which have been prepared by the isocyanate polyaddition process from polyhydroxy compounds and polyisocyanates and which contain incorporated in the molecule two or more groups of the formula



in which the phosphorus atom is linked to a carbon atom directly or through an oxygen or nitrogen atom are reacted at temperatures of  $-20^{\circ}$  to  $250^{\circ}$  C., preferably  $20$  to  $150^{\circ}$  C., with compounds which may be resinous and which contain at least two azomethine groups in the molecule.

The process according to the invention is new and leads to hitherto unknown classes of cross-linked polyurethane plastics.

The linear or branched polyurethanes used as starting materials for the process according to the invention, which contain several groups of the formula

$\begin{array}{c} \text{O} \\ || \\ -\text{P}- \\ | \\ \text{H} \end{array}$  in the molecule, may be obtained in known manner by the reaction of poly-

isocyanates with linear or branched condensation—and or polymerisation products containing hydroxyl groups and having a molecular weight above 1000, and/or compounds containing at least two hydrogen atoms reactive with isocyanates and having a molecular weight below 1000, either the linear or branched condensation and/or polymerisation products containing hydroxyl groups and having a molecular weight above 1000 or the compound containing at least two hydrogen atoms reactive with isocyanates and having a molecular weight below 1000 or both containing at least one

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group of the formula  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—P—} \\ \text{H} \end{array}$  in the molecule.

Where only compounds having a molecular weight above 1000 or only compounds having a molecular weight below 1000 are used for the production of the

non-cross-linked polyurethane, the presence of  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—P—} \\ \text{H} \end{array}$  groups in these compounds, is,

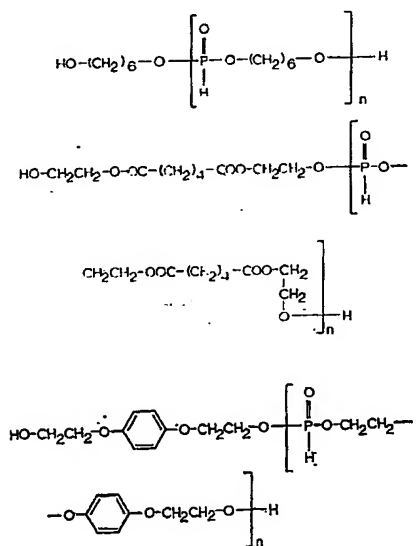
5 of course, essential.

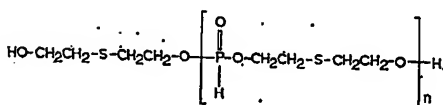
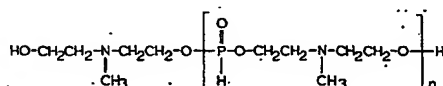
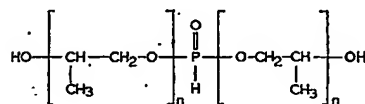
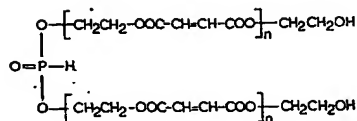
Suitable linear or branched condensation—and/or polymerisation products containing hydroxyl groups and having a molecular weight above 1000 and containing at

least one group of the formula  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—P—} \\ \text{H} \end{array}$  in the molecule include, for example, condensa-

10 tion products, containing terminal hydroxyl groups, of lower dialkylphosphites such as dimethyl-, diethyl-, dibutyl-, or dihexylphosphite or diphenylphosphite and high molecular weight polyester amides, polyacetals or linear or branched polyesters such as are known to be obtainable by thermal condensation of ethylene, glycol, diethylene glycol, propylene glycol, butylene glycol, hexanediol, hexanetriol, glycerol, trimethylpropane, pentaerythritol and adipic acid, phthalic acid, terephthalic acid, maleic acid, fumaric acid or glutaconic acid. Also suitable are the corresponding condensa-  
15 tion products, containing terminal hydroxyl groups of lower dialkylphosphites of the above mentioned type and polyethers, e.g. ethylene oxide-, propylene oxide- or tetrahydrofuran polymers, or polythioethers, e.g. polythiodiglycol. In addition one may also use the polycondensation products of lower dialkyl phosphites and low molecular weight polyhydroxy compounds such as ethylene glycol, propylene glycol, butanediol, hexanediol, hexanetriol, glycerol, mannitol, diethylene glycol, tripropylene glycol, thiodiglycol, N-methyl-diethanolamine, triethanolamine, 2,2-dimethylpropanediol, cyclohexane-1,4-diol, di-β-hydroxyethoxybutane, 1,5-naphthylenedi-β-hydroxyethylether, the di-β-hydroxyethyl ester of adipic acid, phthalic acid, succinic acid or maleic acid, adipic acid-di-β-hydroxypropylamide and di-4-hydroxybutylurea, which poly-  
20 condensation products have a molecular weight above 1000.

25 All these condensation products can be obtained simply by heating the lower dialkylphosphites with the stated high molecular weight or low molecular weight polyhydroxy compound, the lower alkyl radicals contained in the phosphites being split off in the form of the corresponding alcohols. Some of these polycondensation products are represented by the following equation formulae:—  
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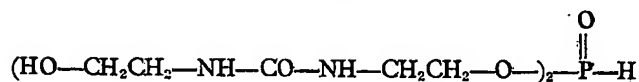
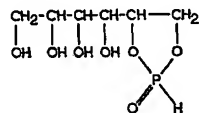
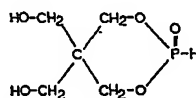
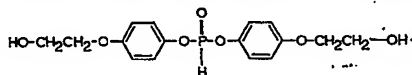


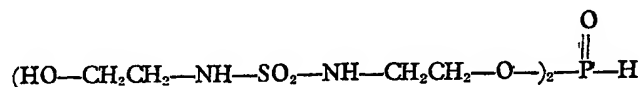
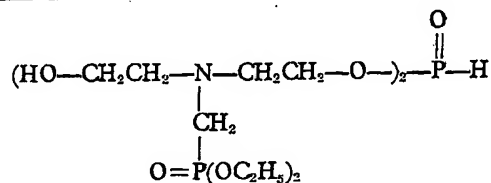
5 In these formulae  $n$  is an integer from 5 to 100.

Suitable compounds containing at least two hydrogen atoms, reactive with isocyanates and having a molecular weight below 1000 and containing one or more

groups of the formula  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—P—} \\ \text{H} \end{array}$  in the molecule include for example, the condensation

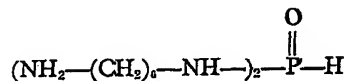
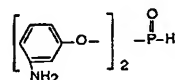
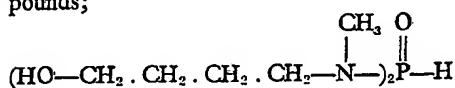
products, containing terminal hydroxyl groups, of lower dialkylphosphites and low molecular weight polyhydroxy compounds of the above-mentioned type. In the same way as the corresponding high molecular weight condensation products, they can be prepared by heating the lower dialkyl phosphites with the stated low molecular weight polyhydroxyl compounds, the lower alkyl radicals contained in the phosphites being split off in the form of the corresponding alcohols, and condensation products having a molecular weight below 1000 being obtained by suitable choice of the molar ratios of the reactants. Some of these condensation products correspond to the specific formulae specified above in which  $n$  in this case represents a number from 1 to 5. Some further examples are represented by the following compounds:



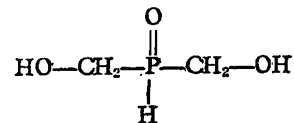
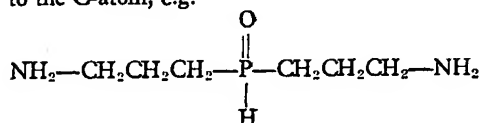


Low molecular weight reaction products of phosphorous acid and alkylene oxides, which contain terminal hydroxyl groups, are also to be mentioned in this connection.

Condensation products of esters, amides or chlorides of trivalent phosphorus with amino alcohols or polyamines, which contain terminal hydroxyl or amino groups, are also suitable. Compounds containing terminal amino groups are only condensed in admixture with a polyhydroxy compound. The following are examples of such compounds;



Also to be mentioned are compounds in which the  $\text{-P(=O)-H}$  group is directly linked to the C-atom, e.g.



For the preparation of the linear or branched polyurethanes used as starting materials for the process of the invention, which contain in the molecule several groups of the

formula  $\text{-P(=O)(H)-}$ , one may use in addition to the above listed linear or branched poly-

hydroxy compounds containing  $\text{-P(=O)(H)-}$  groups and having a molecular weight above

1000 and/or the above mentioned compounds containing at least two hydrogen atoms

reactive with isocyanates and at least one  $\text{-P(=O)(H)-}$  group and having a molecular weight

below 1000, the usual linear or branched polyhydroxyl compounds having a molecular weight above 1000, such as polyesters, polyethers, polythioethers, polyester amides or polyacetals, and the usual compounds containing at least two hydrogen atoms reactive

with isocyanates and having a molecular weight below 1000, such as water, butanediol, trimethylolpropane, glycols containing urea, urethane-, carbonamide-, tertiary amino- and ester-groups, glycols having aromatic ring systems, o-dichlorobenzidine, and 3,3'-dichlorodiaminodiphenylmethane.

For the preparation of the linear or branched, non-cross-linked polyurethanes used as starting materials, one may use any of the known polyisocyanates, such as tetramethylene diisocyanate, hexamethylenediisocyanate and the biuret polyisocyanates well known to be obtainable from hexamethylenediisocyanate by the addition of water, 1,4-cyclohexanediisocyanate, 4,4'-dicyclohexylmethane-diisocyanate, xylylenediisocyanate, 1-(3-isocyanate-phenyl)-ethyl isocyanate, toluylene diisocyanates, phenylene diisocyanates, 1,5-naphthylenediisocyanate, 4,4'-diphenylmethane diisocyanate and 4,4',4''-triphenylmethane triisocyanate, thiophosphoric acid-tri (4-isocyanate-phenylester) as well as polyisocyanates of the above type substituted by a very wide variety of substituents such as alkyl-, alkoxy- or nitro groups or halogen atoms; in addition one may also use the reaction products of the above isocyanates with less than equivalent quantities of polyhydroxyl compounds such as trimethylolpropane, hexanetriol, glycerol or butane diol, as well as polyisocyanates which are masked, for example, with phenols, and polymerised isocyanates having isocyanurate rings.

The preparation of suitable linear or branched polyurethanes from the above mentioned components for the reaction with polyazomethines by the process according to the invention can be carried out by various methods. For example, the linear condensation and/or polymerisation products which contain hydroxyl groups and have a molecular weight above 1000 can be reacted with an excess, based on the terminal groups, of a polyisocyanate, and the resulting adducts which contain free NCO groups can be reacted in such a manner with a compound containing two reactive hydrogen atoms and having a molecular weight below 1000 so that the isocyanate groups are almost completely used up; in this process, a slight excess of reactive hydrogen atoms may be desirable.

Alternatively, the condensation and/or polymerisation products which contain hydroxyl groups and have a molecular weight about 1000 can be mixed with the compounds which contain two reactive hydrogen atoms and have a molecular weight below 1000, and a quantity of diisocyanate equivalent to the sum of the reactive hydrogen atoms present may be added although an excess or a less than equivalent amount of the diisocyanate may be employed, if desired.

According to another method, the condensation and/or polymerisation products which contain hydroxyl groups and have a molecular weight above 1000 can simply be reacted with the equivalent quantity of a diisocyanate, but here again the diisocyanate may be used in slight excess or in slightly less than the equivalent amount.

Lastly, compounds containing at least two hydroxyl groups in the molecule and having molecular weights below 1000 can be reacted with equivalent, less than equivalent or greater than equivalent quantities of polyisocyanates to form polyurethanes.

In all these cases, care is to be taken to ensure that a polyhydroxy compound having a molecular weight above 1000 and/or a compound having at least two reactive hydrogen atoms and a molecular weight below 1000 is used which contains the group

of the formula  $\begin{array}{c} \text{O} \\ | \\ \text{—P—} \\ | \\ \text{H} \end{array}$ , which has been more closely defined, at least once in the molecule.

The reaction products obtained are linear or branched polyurethanes. They are not cross-linked and are therefore soluble in many solvents such as methyl glycol ether acetate, dimethylformamide, N-methylpyrrolidone or cresols. In the undiluted state, these products are viscous oils or more or less hard, thermoplastic materials.

According to the process of the invention, these linear or branched polyurethanes are reacted at  $-20^{\circ}\text{C.}$  to  $250^{\circ}\text{C.}$ , preferably 20 to  $150^{\circ}\text{C.}$ , with compounds, which may be resinous, containing at least two azomethine groups in the molecule.

Such compounds are, for example, di- or trifunctional Schiff's bases derived from monoaldehydes and ketones, such as isobutyraldehyde, cyclohexanone, benzaldehyde or substituted benzaldehydes or chloral with polyamines such as tetramethylene diamine, hexamethylene diamine, 4,4'-diamino-dibutylether, 2,2'-diamino-di-n-propylether, 3,3'-diamino-dipropylsulphone, 1,1,1-tri-(2'-amino-1'-propoxymethyl)-propane, methyl-bis-(3-aminopropyl)-amine, m-phenylenediamine, p-phenylenediamine, 4,4'-diaminodiphenyl, 4,4'-diaminophenylether, 4,4'-diaminodiphenylmethane and

-propane, 4,4' - diaminodiphenylsulphide and -sulphone, 4,4',4'' - triamino-triphenylmethane and 4,4',4''-triaminotriphenylphosphate or -thiophosphate.

In addition, polyfunctional Schiffs' bases derived from lower primary alkyl- and hydroxyalkyl amines, such as methyl, ethyl-, propyl, butyl- or butylamine, ethanol- or propanolamine or anilines and polyaldehydes such as terephthalic dialdehyde may be used as may also polyazomethines derived from polyaldehydes and polyamines of the above mentioned type.

Resinous compounds having a molecular weight of about 2000 to 50,000 and containing at least two azomethine groups may also be mentioned, eg. polyurethanes which contain azomethine groups and which are obtainable from Schiffs' bases with hydroxyl- and/or amino groups by reaction with polyisocyanates and/or masked isocyanates if desired with the use of polyvalent hydroxy compounds such as alcohols, polyesters or polyethers. In this case, the polyisocyanates can equally well be monomers or polyester isocyanates or polyether isocyanates. Schiffs' bases containing hydroxyl- and/or amino groups are, for example, isobutyraldehyde-3-hydroxypropylamine, 4-hydroxy-cyclohexanone-n-butylimine, 4-hydroxy-cyclohexanone-3'-hydroxypropylime, hydroxypivalic, aldehyde-(2-hydroxy-ethyl- and 3-hydroxy-1-propyl)imine, &&-dimethyl-&-hydroxy-butyraldehyde-(2-hydroxyethyl and 3-hydroxy-1-propyl)-imine, 4-hydroxy-cyclohexanone-(2-hydroxyethyl- and 3-hydroxy-1-propyl)-imine and p-(1-hydroxyethoxy)-benzaldehyde-(2-hydroxyethyl- and 3-hydroxyethyl)-imine.

It is also possible to produce the polyazomethines from the necessary components, i.e. from monoaldehydes or ketones and polyamines or from polyaldehydes and mono- or polyamines of the above mentioned type in the reaction mixture. In that case, an aldehyde or ketone and a polyamine or polyaldehyde and/or a mono- or polyamine are added either simultaneously or successively to the linear or branched

polyurethane which contains two or more  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{H} \end{array}$  groups in the molecule. The poly-

azomethine obtained then reacts in situ with the  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{H} \end{array}$  groups of the polyurethane,

undergoing cross-linking in the process.

To achieve a high degree of cross-linking, the quantitative proportion of polyurethane and polyazomethine is preferably so chosen that one azomethine group reacts

on each  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{H} \end{array}$  group present in the polyurethane. If a lesser degree of cross-linking is desired, the polyazomethine is used in less than equivalent quantity. Excess quantities

of polyazomethine based on the number of  $\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}- \\ | \\ \text{H} \end{array}$  groups present may also be used.

The cross-linking, according to the invention, of the linear or branched polyurethane may be carried out in bulk, e.g. by mixing the polyazomethine into the thermoplastic polyurethane on a rubber mixing roller, at room temperature. Fillers such as carbon black or colloidal silicic acid or lubricants such as stearic acid may be incorporated at the same time. Cross-linking then proceeds subsequently or simultaneously with a forming operation using the vulcanisation conditions usual in the rubber industry at temperatures of about 100° C. or more.

If the linear or branched polyurethane is present in solution, as, for example, is customary for the production of lacquers and coating materials, the polyazomethine can be mixed either in bulk or as a solution with the solution of the polyurethane, and lacquer coatings can then be applied from this mixture. Depending on the concentration

of the  $\begin{array}{c} \text{O} \\ \parallel \\ \text{—P—} \\ | \\ \text{H} \end{array}$  groups in the polyurethane and the reactivity of the polyazomethine,

the lacquer solutions may dry even at room temperature, undergoing cross-linking, or only harden when stoved at temperatures of 80 to 180° C.

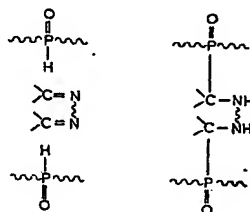
To produce pourable moulding compositions, the molten polyurethane can be mixed hot with the polyazomethine, the mixture poured into suitable moulds and the moulded articles hardened at elevated temperature.

To produce press moulded articles, the polyurethane is mixed with relatively large quantities of fillers such as sawdust, chalk, carbon black or colloidal silicic acid and a polyazomethine and the mixture formed by pressure moulding at elevated temperature.

If desired, for cross-linking the polyurethane, polyisocyanates such, for example, as dimerised or trimerised toluylene-2,4-diisocyanate may be used in addition to the polyazomethine which is used according to the invention.

Depending on the choice of starting materials and reaction conditions, high grade rubbery elastic materials, coatings, films, foils, compression moulded articles, adhesive bondings and textile coatings can be obtained by the process of the invention.

The cross-links between the polyurethane chains, which are brought about by phosphorus-carbon bonds according to the following idealised scheme or formulae, are thermally very stable, with the result that the products of the process are distinguished by high heat resistance.



Because they have a proportion of chemically bound phosphorus, the products of the process have the additional advantage of being difficult to ignite or combust. The following examples illustrate the invention:—

#### EXAMPLE 1

a) Preparation of the starting material. 50 g of a linear polyester of adipic acid and ethylene glycol of molecular weight 2000 and OH number 56 are dissolved in 100 ml of dimethylformamide. To this solution are added 47.6 g of diphenylmethane-4,4'-diisocyanate at 100° C., and the mixture is then heated for 30 minutes at 130 to 140° C. It is then cooled to 100° C. and there are added 50 g of di-(6-hydroxyhexyl)-phosphite which was prepared by condensing 1 mol diethylphosphite with 2 mols hexane-diol. When the exothermic reaction has died down, the solution is heated for another 30 minutes at 130° C. and a sample of this solution is then painted on a glass plate to form a film (film A).

b) Process according to the invention. 24.8 g of the di-Schiffs' base of 2 mols benzaldehyde and 1 mol hexamethylenediamine are introduced at 100° C. into the clear, colourless polyurethane solution prepared according to a), and a sample of the solution thus obtained is painted on a glass plate (film B). The glass plates with films A and B are dried for 12 hours at 100° C. After this treatment, film A obtained from the starting material still has a sticky, honey-like consistency and dissolves readily and completely in cold dimethylformamide whereas Film B obtained by the process according to the invention has hardened to a completely non-sticky material which is clear, elastic and insoluble in dimethylformamide. The polyurethane solution left after film B has been painted swells after 3 hours' storage at room temperature, which shows that cross-linking of the polyurethane with the di-Schiffs' base also proceeds at room temperature.

#### EXAMPLE 2

a) Preparation of the starting material. 100 g of a linear polyester of adipic acid and ethylene glycol (molecular weight 2000, OH number 56) are dissolved in 100 ml dimethylformamide and reacted at 100° C. with 33.5 g diphenylmethane-4,4'-diiso-

b) Process according to the invention. 14.6 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine are added at 100° C. to the solution prepared according to a), and the resulting solution is painted on to a glass plate. The glass plate is heated for 12 hours at 100° C. At the end of this treatment, the polyurethane film is clear, elastic and insoluble in dimethylformamide. The film has high surface glass and remarkably firm adhesion to the glass surface.

10 a) Preparation of the starting material. The procedure is exactly analogous to Example 2a) except that 22.5g hexamethylenediisocyanate are used instead of 33.5 g diphenylmethane-4,4'-diisocyanate. 10

b) Process according to the invention. The solution prepared according to a) is reacted in the manner described in Example 2b) with 14.6 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine and a film of this solution is painted on to a glass plate. After 12 hours' hardening at 100° C., an elastic soft, colourless film is obtained which is no longer soluble in boiling dimethylformamide.

20 a) Preparation of the starting material. 50 g of a linear polypropylene glycol of molecular weight 2000 and OH number 56 are dissolved in 100 ml glycol monomethyl-ether acetate and reacted with 47.6 g diphenylmethane-4,4'-diisocyanate at 130° C. 50 g di-(6-hydroxyhexyl)-phosphite are then added at 100° C., the mixture is then heated for another 30 minutes at 130° C. and finally a sample of the resulting milky turbid solution is painted on to glass (film A).

25 b) Process according to the invention. 24.8 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine are added at 100° C. to the solution prepared according to a), and a film is painted on to a glass plate (film B). The two glass plates with films A and B are heated for 10 hours at 100° C. After this treatment, the film A made from the starting material has a turbid, cheesy consistency and is readily  
30 soluble in dimethylformamide whereas film B which has been cross-linked according to the invention is soft and colourless and has a glossy surface.

a) Preparation of the starting material. A mixture of 207 g di-( $\beta$ -chloroethyl)-phosphite and 125 g of 1,6-hexanediol is condensed in a vacuum at 130° C. 147 g of ethylene chlorohydrin are distilled off in the course of 5 hours at 130° C. Condensation is continued at 150° C. in a vacuum until the calculated quantity (161 g) of ethylene chlorohydrin has been split off. The condensation product (170 g) is a linear polyester of phosphorous acid (molecular weight 2100; OH number 54). 20 g of this polyester are dissolved in 20 ml dimethylformamide. 2.4 g diphenylmethane-4,4'-diisocyanate are added to this solution at 120° C. and the reaction mixture then heated for a further 30 minutes at 130° C., and a film is then made from a sample of this solution on a glass support (film A);

b) Process according to the invention. 16 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine are added at room temperature to the polyurethane solution prepared according to a), and a film is immediately painted on to a glass plate. The remaining polyurethane solution undergoes cross-linking even after only a few minutes to form a gelatinous mass. The two films A and B are heated for 6 hours at 100° C. At the end of this treatment, film A obtained from the starting material has a honey-like consistency and is cloudy while film B which has been cross-linked according to the invention is clear, scratch-resistant and very hard. Film B has a glossy surface and adheres very firmly to the glass support.

a) Preparation of the starting material. A mixture of 750 g triethylene glycol and 828 g dichloroethyl phosphite is heated to 120 to 140° C. under reduced pressure. 628 g ethylene chlorohydrin are split off in the course of 8 hours. 950 g of a colourless, oily polyester (OH number 132) remain behind in the residue.

11.4 g hexamethylenediisocyanate are added to 55 g of this polyester at 120° C. The viscous, colourless reaction product is then dissolved in 50 ml dimethylformamide and a film is made from a sample of this solution on a glass support (film A).

60 b) Process according to the invention. 19 g of the di-Schiff's base of benzaldehyde and hexamethylene diamine are added at 100° C. to the polyurethane solution



prepared according to a), and a film of this solution is then painted on a glass plate (film B). The two glass plates with films A and B are kept at 110° C. for 12 hours. At the end of this time, film A prepared from the starting material is still liquid, cloudy and not cross-linked whereas film B, although soft, is elastic and clear and insoluble in dimethylformamide.

## EXAMPLE 7

a) Preparation of the starting material. By a procedure analogous to that described in Example 6a), a linear polyester (OH number 151) is prepared from 590 g 1,6-hexanediol and 828 g dichloroethylphosphite.

22 g diphenylmethane -4,4'-diisocyanate are added at 100° C. to a solution of 50 g of this polyester and 50 g of a linear polypropylene glycol (molecular weight 2000; OH number 54) in 100 ml dimethylformamide and the reaction mixture is then heated for one hour at 130° C.

b) Process according to the invention. 19 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine are added at 20° C. to the colourless polyurethane solution prepared according to a), and a sample of the solution is then spread over a smooth wooden plate. The plate is dried for 10 hours at 100° C. At the end of this time the lacquer film is completely cross-linked. It is scratch-resistant, colourless, clear and of high gloss. The modified polyurethane solution remaining behind after application of the film keeps unchanged for 2—3 days at room temperature; at the end of that time, the polyurethane slowly cross-links in solution to form a colourless, gelatinous mass.

## EXAMPLE 8

a) Preparation of the starting material. 50 g of the phosphite polyester (OH number 151) prepared according to Example 7a) together with 50 g of a polyester (molecular weight 2000; OH number 56) prepared from adipic acid and ethylene glycol are dissolved in 100 ml dimethylformamide. 15.5 g of a mixture of 65% toluylene-2,4-diisocyanate and 35% toluylene-2,6-diisocyanate are added to this solution at 100° C. When the exothermic reaction has subsided the solution is heated for one hour at 130° C. From a sample of this solution, a film is spread onto a glass plate (film A).

b) Process according to the invention. The polyurethane solution prepared according to a) is divided into two equal parts. 19 g of the di-Schiffs' base of benzaldehyde and hexamethylene diamine are stirred into one part and a film is painted on a glass plate (film B). 9.5 g of the same di-Schiffs' base is stirred into the other part of the solution and a film (film C) is made in an analogous manner. Films A, B and C are heated for 12 hours at 100° C. At the end of that time, film A still has a sticky, honey-like consistency, film B is soft elastic and glossy and film C is elastic but not completely free from stickiness.

## EXAMPLE 9

a) Preparation of the starting material. A polyurethane solution is prepared as in Example 8a) except that 15.0 g hexamethylene diisocyanate are used instead of 15.5 g toluylene diisocyanate.

b) Process according to the invention. 14.5 g of the di-Schiffs' base of 2 molecules of isobutyroaldehyde and 1 molecule of hexamethylenediamine are added at 25° C. to the polyurethane solution prepared according to a), and a film of this solution is then painted on to a polished copper plate. The plate is heated for 12 hours at 120° C. The cross-linked film is clear, non-sticky and elastic and has a pale yellow colour.

## EXAMPLE 10

a) Preparation of the starting material. 33.8 g diphenylmethane-4,4'-diisocyanate are added at 130° C. to a solution in 100 ml dimethylformamide of 100 g of the polyester (OH number 151) prepared according to Example 7a), and the solution is then stirred for 3 hours at 120° C.

b) Process according to the invention. The solution prepared according to a) is divided into two equal parts. 38 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine are added to one part, and a film is painted on a glass plate (film A). The other part of the solution is mixed with 19 g of the same di-Schiffs' base and a film (film B) is painted. The two films are heated for 12 hours at 100° C., and both films are then hard, scratch-resistant, elastic and glossy.

## EXAMPLE 11

a) Preparation of starting material. The procedure is the same as in Example

10a) except that 22.7 g hexamethylene diisocyanate are used instead of 33.8 g diphenylmethane-4,4'-diisocyanate.

- 5 b) Process according to the invention. The polyurethane solution obtained according to a) is mixed with 38 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine at 100° C. A film is cast on to a glass plate with a sample of the solution. After 12 hours' drying at 100° C. the resulting film is clear, elastic and scratch resistant and is remarkable for its extraordinarily firm adhesion to the glass surface. 5

#### EXAMPLE 12

- 10 a) Preparation of the starting material. 50 g of a linear polyester of adipic acid and ethylene glycol (molecular weight 2000; OH number 56) are dissolved in 100 ml dimethylformamide and reacted with 32 g hexamethylene diisocyanate at 130° C. The reaction is allowed to proceed for 30 minutes at 130° C. 50 g di-(6-hydroxyhexyl)-phosphite are then added and the solution then heated for one hour at 130° C. 10

- 15 b) Process according to the invention. The polyurethane solution obtained according to a) is mixed at room temperature with 19 g of the di-Schiffs' base of 2 molecules isobutyraldehyde and 1 molecule hexamethylenediamine. From this modified solution, films are poured on to glass plates and dried for 8 hours at 100° C. After this treatment, the films are clear, elastic and insoluble in dimethylformamide. 15

#### EXAMPLE 13

- 20 a) Preparation of the starting material. 50 g of the polyester (OH number 151) prepared according to Example 7a) are dissolved in 50 ml dimethylformamide. 14.2 g naphthylene-1,5-diisocyanate are stirred into the solution at 130° C. and the solution is kept at a temperature of 130° C. for one hour. 20

- 25 b) Process according to the invention. 38 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine are added at 100° C. to the solution obtained according to a), and a film is painted on a glass plate. After 6 hours' drying at 100° C., an opaque, pale yellow film is obtained which is extraordinarily hard and scratch-resistant. 25

#### EXAMPLE 14

- 30 a) Preparation of the starting material. A mixture of 414 g dichloroethylphosphite and 790 g diphenylolpropane-di-( $\beta$ -hydroxyethylether) is condensed in vacuo, first at 140° C. and finally at 160° C. until all the ethylene chlorohydrin has been split off. 880 g of a yellow, clear, highly viscous resin remain in the residue. 30

- 35 52.8 g of this polyester are dissolved in 50 ml dimethylformamide and reacted at 130° C. with 5 g hexamethylene diisocyanate. The resulting yellow, clear oil is divided into three equal parts. 35

- 40 b) Process according to the invention. The polyurethane solutions obtained according to a) are treated at 20° C. with 8 g of the di-Schiffs' base of isobutyraldehyde and hexamethylenediamine, 10 g of the di-Schiffs' base of benzaldehyde and hexamethylenediamine and 14 g of the di-Schiffs' base of benzaldehyde and 4,4'-diaminodiphenylmethane respectively. As in the preceding example, films A, B and C are made from the modified solutions and dried at 100° C. for 12 hours. All the films obtained are hard and scratch resistant. Films A and C are yellow, film B is colourless. 40

#### EXAMPLE 15

- 45 a) Preparation of the starting material. The procedure is the same as in Example 14a) except that 2g of naphthylene-1,5-diisocyanate are used instead of 5 g of hexamethylene-diisocyanate. 45

- 50 b) Process according to the invention. The solution obtained according to a) is divided into three parts which are treated, respectively, with the di-Schiffs' bases mentioned in Example 14b). The films obtained are hardened for 12 hours at 100° C. and are then non-sticky, scratch-resistant and opaque. 50

#### EXAMPLE 16

- 55 a) Preparation of the starting material. 628 g N,N-di-( $\beta$ -hydroxyethyl)-aminomethyl-phosphonic acid diethyl ester are condensed with 414 g dichloroethyl phosphite at 110 to 130° C. in vacuo. Ethylene chlorohydrin is split off and a highly viscous, resinous, linear polyester (molecular weight 14000) is formed. Yield 740 g. 55

43.8 g of this polyester are dissolved in 50 ml dimethylformamide. The solution is treated with 7.5 g diphenylmethane-4,4'-diisocyanate and stirred for one hour at 130° C.

- b) Process according to the invention. 30 g of the di-Schiffs' base of benzaldehyde

and 4,4'-diamino-diphenylmethane are added to the polyurethane solution prepared according to a), and films are painted on wood and on glass. The films are dried for 12 hours at 100° C. and are then hard and scratch-resistant. They are brown in colour and insoluble in dimethylformamide.

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## EXAMPLE 17

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500 g of a copolyester of OH number 65, which is prepared from adipic acid and a mixture of 65 mol percent of hexanediol-(1,6) and 35 mol percent of 2,2-dimethylpropanediol-(1,3), are dehydrated in vacuum at 130° C. for 30 minutes. At 90° C. 50 g of di-(6-hydroxyhexyl)-phosphite and subsequently 122 g of diphenylmethanediisocyanate-(4,4') are added with stirring for about 10 minutes. The homogeneous reaction mixture is then heated at 100° C. for 20 hours. A non-cross-linked storable product is obtained which can be processed as such on rubber rollers or in form of a solution in suitable solvents.

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5 g of the di-Schiff's base of 4,4'-diaminodiphenylmethane and 2 mols of benzaldehyde are incorporated on the roller in 100 g each of the rollable polyurethane. A plastic with high-grade rubber elastic properties is obtained by cross-linking the mixture by heating to about 130° C. for 30 minutes while moulding. The properties of the elastic plastic can be modified in any desired manner by techniques known to the art by the additional use of fillers, e.g. carbon black.

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Rubber-elastic films are produced by dissolving for example 30 g of the rollable polyurethane in 70 g of ethyl acetate and adding about 1.2 g of the di-Schiff's base of hexamethylene diamine and 2 mols of benzaldehyde. The solution is cast to give films of any desired thickness which are cross-linked by heating to 130° C. for about 30 minutes after evaporation of the solvent. Films with equally good rubber-elastic properties are also obtained when using as solvent, instead of ethyl acetate, e.g. methylene chloride, chloroform, glycol monomethyl ether acetate, glycol mono ethyl ether acetate, methylisobutylketone, chlorobenzene or dimethylformamide.

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Instead of the above mentioned bifunctional azomethines, 4.4 g of 1,5-dibenzylideneimino-naphthalene, 4.8 g of 1,6-di-(4'-chlorobenzalimino)-hexane, 5 g of 1,6-di-(4'-nitrobenzalimino)-hexane or 5.9 g of 4,4'-di-(4''-chlorobenzylidene-imino)-diphenylmethane can be used as cross-linking agent per 100 g each of the rollable polyurethane.

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## EXAMPLE 18

As described in Example 17, a rollable polyurethane is prepared from 500 g of a polyester of adipic acid and a mixture of 65 mol percent of hexanediol-(1,6) and 35 mol percent of 2,2-dimethylpropanediol-(1,3) (OH number 65), 100 g of di-(6-hydroxyhexyl)-phosphite and 113 g of toluylene diisocyanate-(2,4) or readily accessible mixtures thereof with toluylene-diisocyanate-(2,6).

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For cross-linking this product as described in Example 17, 6.7 g of the di-Schiff's base of hexamethylene diamine and 2 mols of benzaldehyde or an equivalent amount of one of the other Schiff's bases mentioned in Example 17 are used per 100 g each of the polyurethane.

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## EXAMPLE 19

A polyurethane prepared from 500 g of a polyester of adipic acid, 65 mol percent of hexanediol-(1,6) and 35 mol percent of 2,2-dimethyl-propanediol-1,3 (OH number 65), 150 g of di-(6-hydroxyhexyl)-phosphite and 208 g of diphenylmethane diisocyanate-(4,4') is suitable to produce a cross-linked plastics and coatings as described in Example 17, with 9 g of the bifunctional azomethine of hexamethylene diamine and 2 mols of benzaldehyde per 100 g each of the polyurethane.

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## EXAMPLE 20

500 g of polybutylene glycol (OH number 42) are dehydrated at 130° C. for 30 minutes in a water-jet vacuum pump. At 90° C. 50 g of di-(6-hydroxyhexyl)-phosphite and 68 g of hexamethylene diisocyanate are added with stirring for about 10 minutes. The reaction mixture is subsequently heated at 100° C. for 20 hours. A rollable polyurethane is obtained which can be cross-linked as described in Example 17 with 4.2 g of 1,6-dibenzalimino-hexane per 100 g each of the product.

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## EXAMPLE 21

500 g of a polyester of adipic acid and a mixture of 65 mol percent of hexanediol-(1,6) and 35 mol percent of 2,2-dimethylpropanediol-(1,3) (OH number 65) are dehydrated in vacuum at 130° C. for 30 minutes. At 90° C. 100 g of di-(6-hydroxy-

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hexyl)-phosphite, 221 g of diphenylmethane diisocyanate-(4,4') and 22.5 g of butanediol-(1,4) are stirred in successively stirred within a total of 10 minutes. The mixture is then heated at 100° C. for 20 hours. 30 g of the resulting polyurethane are dissolved in 70 g of glycol monomethylether acetate. To this solution there are added 1.8 g of the bifunctional base of hexamethylene diamine and 2 mols of benzaldehyde or an equivalent amount of one of the other azomethines mentioned in Example 17. Films are then prepared from the solution by painting. After evaporation of the solvent the non-cross-linked films are cross-linked by heating at 130° C. for one hour. The cross-linked films exhibit outstanding elastic properties and are insoluble in conventional solvents.

#### EXAMPLE 22

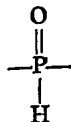
20 g of a polyphosphite of mean molecular weight 774, which is prepared by ester interchange of diethylphosphite with hexanediol-(1,6) at the molecular ratio 5:4, 52 g of diphenylmethane diisocyanate-(4,4') and butanediol-(1,4) are stirred in 100 g of a polyester of adipic acid and a mixture of 65 mol percent of hexanediol-(1,6) and 35 mol percent of 2,2-dimethylpropanediol-(1,6) (OH number 65) after dehydration at 90° C. The mixture is heated at 100° C. for 20 hours to obtain a rollable polyurethane which can be cross-linked with a di-Schiff's base as described in Example 21.

#### EXAMPLE 23

The experiment of Example 22 is repeated, using however instead of the polyphosphite of the mean molecular weight 774, 20 g of a polyphosphite which is prepared in similar manner, having a mean molecular weight of 2100 and 48 g of 4,4'-diphenylmethane diisocyanate. The polyurethane obtained after heating can be dissolved in glycol monomethylether acetate and can be processed after the addition of 6 g of the Schiff's base of hexamethylene diamine and 2 mols of benzaldehyde per 100g each of solid to give rubber-elastic films.

#### WHAT WE CLAIM IS:—

1. A process for the preparation of high molecular weight, cross-linked polyurethane plastics, in which linear or branched polyurethanes which have been prepared by the isocyanate polyaddition process from polyhydroxyl compounds and polyisocyanates and which contain, incorporated in the molecule, two or more groups of the formula:—



in which the phosphorus atom is linked to a carbon atom either directly or through an oxygen or a nitrogen atom, are reacted at a temperature of -20° C. to +250° C. with a compound which may be resinous which contains at least two azomethine groups in the molecule.

2. A process as claimed in claim 1 in which a temperature of from 20 to 150° C. is used for the reaction.

3. A process as claimed in claim 1 or claim 2 in which the compound which contains at least two azomethine groups in the molecule is produced *in situ* in the reaction mixture from aldehydes or ketones and polyamines or from polyaldehydes and monoamines or polyamines in the reaction mixture.

4. A process as claimed in any of claims 1 to 3 including the step of shaping the polyurethane.

5. A process as claimed in claim 1 substantially as herein described with reference to any of Examples 1 to 16.

6. A process as claimed in claim 1 substantially as herein described with reference to any of Examples 17 to 23.

7. Cross linked polyurethanes when prepared by the process of claims 1 to 5.

8. Cross linked polyurethanes when produced by the process of claim 6.

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